Tertiarybutyldimethylantimony: A new Sb source for low-temperature organometallic vapor phase epitaxial growth of InSb

C. H. Chen and G. B. Stringfellow
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

D. C. Gordon, D. W. Brown, and B. A. Vaartstra
Advanced Technology Materials, Inc., 7 Commerce Drive, Danbury, Connecticut 06810

(Received 10 February 1992; accepted for publication 21 April 1992)

III-V semiconductors such as InAsSb, InSbBi, and InAsSbBi are useful materials for far-infrared applications. Their growth usually requires low temperatures. The standard Sb source, trimethylantimony (TMSb), decomposes very slowly at low temperatures. In this work, a new Sb source, tertiarybutyldimethylantimony (TBDMSb), is investigated for OMVPE growth of InSb. Good surface morphology InSb layers were obtained for growth temperatures from 450 to as low as 325 °C. The growth temperature can be lowered by more than 100 °C when TBDMSb replaces TMSb. The growth efficiency of InSb using trimethylindium (TMIn) and TBDMSb is on the order of 1×10^4 μm/mole. The high values of growth efficiency indicate that there is neglectible parasitic reaction between TMIn and TBDMSb. The results indicate that TBDMSb is an excellent replacement for TMSb and TIPSb in the growth of Sb-containing alloys.

Sb-containing alloys have the lowest energy band gaps among the conventional III-V semiconductors.[1] They are important materials for infrared applications. In the past, high-quality Sb-containing III-V semiconductors have been grown by organometallic vapor phase epitaxy (OMVPE) mainly using trimethylantimony (TMSb).[2,3] For some special applications, however, the TMSb decomposition temperature is too high. For example, Bi is added to InAsSb in order to produce materials with absorption at 12 μm for far-infrared applications.[4,5] Bi concentrations of greater than 6% have been obtained in InAsBi alloys,[5] with a reported reduction in the energy band gap of 55 meV per percent Bi.[4] However, growth temperatures as low as 275 °C are required.[5] At this low temperature, TMSb decomposes very slowly.[6] Thus, other Sb sources are required for low-temperature growth.

Beside TMSb, triethylantimony (TESb) has occasionally been used for the growth of Sb-containing materials.[7,8] Biefeld and Hebner[8] reported the growth of InSb using TESb at 400 °C with a V/III ratio of 2.4. However, TESb is probably too stable for growth at low temperatures. The bond strength for hydrocarbons decreases as follows:[9]

H-methyl > H-ethyl > H-isopropyl.

Thus, TESb is expected to decompose at higher temperatures than required for triisopropylantimony (TIPSb). Since TIPSb is not suitable for low-temperature growth, as discussed below, TESb is not a promising candidate.

We have recently investigated several Sb precursors for this purpose, including trivinylantimony (TVSb),[10] TIPSb,[11] and triallylantimony (TASb).[11] TVSb is too too stable for it to be useful for low-temperature growth.[10] On the other hand, TASb is too labile: It apparently decomposes slowly during storage at room temperature.[12] To date, only TIPSb has been successfully used to grow InSb at temperatures as low as 300 °C.[13,14] However, this is achieved only when high V/III ratios are used.[14]

In this work, we report the use of the newly developed Sb source, tertiarybutyldimethylantimony (TBDMSb), as a replacement for TMSb in the OMVPE growth of Sb-containing alloys.

TBDMSb has a vapor pressure of 7.7 Torr at 23 °C.[15] This value is much higher than the 0.5 Torr for TIPSb at the same temperature. Thus, TBDMSb is more convenient than TIPSb. The decomposition study of TBDMSb[15] has shown that the value of T_{50} is 300 °C in both He and D_2 ambients, much lower than for TMSb. Thus, it is expected that the temperature for OMVPE growth of InSb and related alloys can be reduced by replacing TMSb with TBDMSb. In fact, the results of this study show that the growth temperature for InSb grown using TBDMSb can be lowered by more than 100 °C as compared to using TMSb, and by about 50 °C as compared to using TIPSb. In addition, the pyrolysis studies indicate that TBDMSb decomposes by a combination of homolysis and disproportionation reactions that apparently occur without the production of free radicals. This suggests that TBDMSb may be used to produce epitaxial layers without high residual carbon doping levels.

The epilayers were grown in an atmospheric-pressure, horizontal OMVPE reactor. The cross section of the rectangular quartz reactor tube is 5-cm wide and 2-cm high. The carrier gas for the liquid and/or solid sources was palladium-diffused hydrogen, with a total flow rate of about 1200 cc/min. Separate stainless-steel tubing was used for the group III and group V reactants in order to minimize possible parasitic reactions.[16] The mixing of the group III and V reactants occurred immediately before entering the quartz reactor. The In source was trimethylindium (TMIn), obtained from CVD incorporated. The TBDMSb source was synthesized by Advanced Technology Materials, Inc.[15] Typical flow rates were 150 cc/min for TMIn held at 0 °C and 2.5–100 cc/min for TBDMSb

 0003-6951/92/270204-03$03.00

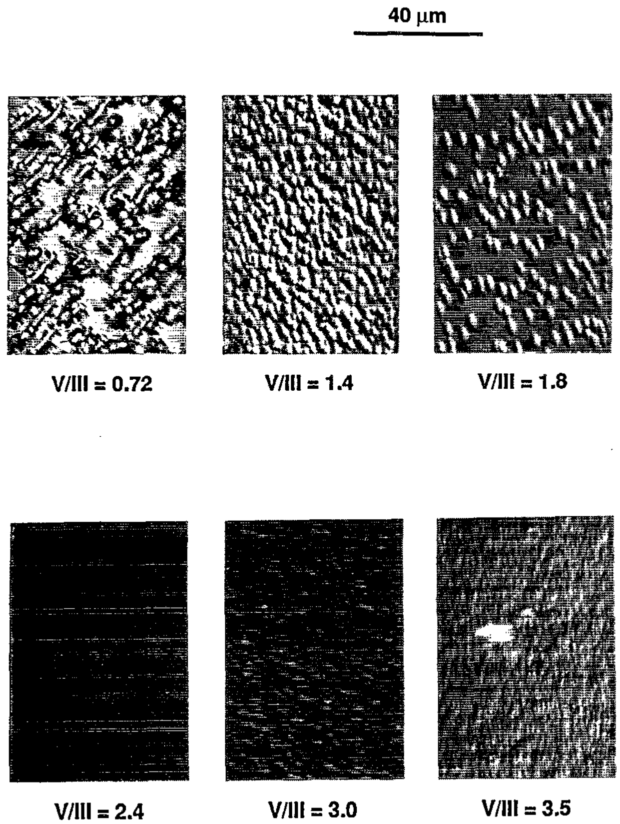

FIG. 1. V/III ratio dependence of InSb surface morphology for layers grown using TBDMSb and TMIn at 400 °C. The epilayer thicknesses are 1.0 μm for V/III=0.72, 1.4 μm for V/III=1.4, 1.4 μm for V/III=1.8, 2.2 for V/III=2.4, 1.8 μm for V/III=3.0, and 2.0 μm for V/III=3.5

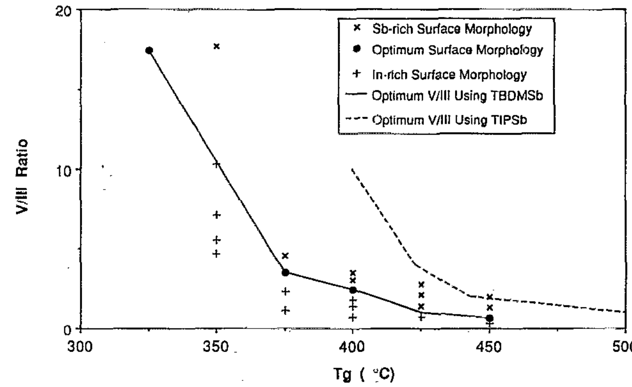

FIG. 2. Summary of InSb surface morphology as a function of both temperature and V/III ratio. The results for InSb grown using TIPSb and TMIn (Ref. 10) are also shown for comparison.

held at 22 °C. The substrates were undoped (100) InSb and semi-insulating (100) InP.

The surface morphologies were observed using a differential interference contrast microscope. Layer thicknesses were determined by observing the heteroepitaxial interface between the epilayer and the InP substrate on a cleaved cross section. The crystallinity of the epilayers was verified using x-ray diffraction for samples grown on InP substrates. The epilayers show well-resolved $K\alpha 1$ and $K\alpha 2$ peaks despite the large lattice mismatch with the InP substrates. Epilayers grown on semi-insulating InP substrates were characterized using the van der Pauw technique. The measurements were carried out at 77 K to eliminate the contribution of intrinsic carriers. The In contacts on the four corners of the rectangular samples were annealed at 300 °C for 90–120 s under a N_2 ambient. The magnetic field was 5 kG and the sample current was between 10 to 100 μA, depending upon the resistivity.

The growth efficiency for InSb from TBDMSb and TMIn is about 1×10^4 μm/mole for temperatures higher than 400 °C. This high value of growth efficiency indicates that there is minimal parasitic reaction between TMIn and TBDMSb.[4,16] For growth temperatures lower than 400 °C, the growth efficiency decreases due to incomplete decomposition of TMIn.[5,13]

Figure 1 shows that the surface morphologies of InSb layers grown on InSb substrates at 400 °C depend strongly on the input V/III ratio. For a low V/III ratio of 0.72, the surface is covered by In droplets. With an increase in V/III ratio to 1.4 and 1.8, the surfaces are less In-rich and hillocks are observed. The hillock density is reduced when the V/III ratio is increased slightly from 1.4 to 1.8. This type of surface morphology will be termed "In-rich." At V/III =2.4, the surface is quite smooth and appears to be shiny to the naked eye, although it is not featureless. This V/III ratio is very close to the optimum value for TBDMSb and TMIn at this temperature. This kind of surface morphology will be called "near-optimum." With a further increase in V/III ratio, the surface morphology deteriorates with the formation of Sb droplets on the surface. This type of surface morphology will be called "Sb-rich."

From Fig. 1, it is clear that only a narrow range of V/III ratio yields good surface morphology InSb layers. This limit is not related to the use of TBDMSb, but to the low vapor pressures of both metallic In and Sb, as has been discussed in detail in Ref. 17. V/III ratios of 0.72, 1.4, and 1.8 are too low: The excess In forms a liquid phase on the surface, leading to vapor-liquid-solid (VLS) three-phase growth.[18,19] The whiskers are difficult to see from the top view in Fig. 1, but they can be readily seen when the samples are examined in cross section. On the other hand, V/III ratios of 3.0 and 3.5 are too high. Since Sb has a melting point of 630 °C, VLS growth does not occur. The excess Sb forms a solid second phase which leads to the growth of hillocks. The In-rich surface morphologies in Fig. 1 become gradually worse as the V/III ratio is reduced. These less-than-optimum surface morphologies still appear to be somewhat shiny to the naked eye. In contrast, the surface morphologies for InSb layers grown using TIPSb at low V/III ratios become very rough and appear to be black to the naked eye.

Similar studies of the V/III ratio dependence of surface morphology have also been carried out at other temperatures. The trend is similar to that shown in Fig. 1, but with a different optimum V/III ratio at each temperature. The results are summarized in Fig. 2. For comparison, Fig. 2 also shows the optimum V/III ratio versus temperature for InSb grown using TIPSb and TMIn in the same reactor.[13] Stauf *et al.*[14] have also reported the growth of InSb using TMIn and TIPSb. However, it is somewhat difficult to make a direct comparison between their results and the present results since the reactor geometries are quite different. The reactor geometry can have a large effect on the decomposition temperature for a precursor due to changes in the time required for the precursor to pass through the heated gas above the substrate.[13] It is seen from Fig. 2 that V/III ratios of close to unity are optimum for InSb grown at 450 °C. This is not surprising because both TMIn and TBDMSb are expected to be completely decomposed.[15,20] As the growth temperature is decreased, the optimum V/III ratio increases. This is similar to the results of InSb grown using TIPSb.[13] The results in Fig. 2 indicate that TBDMSb is not completely decomposed for temperatures lower than about 370 °C. This temperature is somewhat higher than that reported for TBDMSb decomposition in the ersatz reactor.[15] The difference is due to factors such as the residence time in the hot zone and the temperature profile, as discussed in detail previously.[13]

From Fig. 2, it is clear that the growth temperature is as much as 50 °C lower using TBDMSb than for TIPSb. For example, InSb can be grown using TBDMSb with low V/III ratios of 2.4 and 3.5 at 400° and 375 °C, respectively. Even at 350 °C, the optimum value of V/III ratio is still a moderate 15. In comparison, using TIPSb and TMIn, the surface is routinely In-rich for InSb grown at temperatures of less than 400 °C with a V/III ratio of about 20 in the same reactor. Thus, TBDMSb is superior to TIPSb for low-temperature growth. This conclusion is somewhat unexpected since the T_{50} values for TIPSb and TBDMSb decomposition have been reported to be nearly the same under the same conditions.[15] Similar differences in decomposition behavior between ersatz and real OMVPE reactors have been reported previously.[13] For example, the value of T_{50} has been reported be about 325 °C for TMIn[20] and about 300 °C for TIPSb[11] in the ersatz reactor under similar conditions. However, TIPSb apparently decomposes more slowly than TMIn in the OMVPE growth reactor,[13] as seen from the V/III ratio dependence of InSb surface morphology as well as from studies of the separate decomposition of elemental In and Sb on a substrate. Such differences are partially due to differences in the ratios of homogeneous and heterogeneous reactions in the two types of reactors. In the ersatz reactor, TIPSb and TBDMSb decompose homogeneously.[13] For the OMVPE growth in this work, heterogeneous reactions may play a much more important role since the hot zone is confined to a thin boundary layer. This is especially true at low temperatures where heterogeneous decomposition generally becomes dominant.

Figure 2 shows that low V/III ratios can be used for the growth of InSb at temperatures between 375–400 °C. This is significant because it may allow the growth of InAsSbBi alloys with an energy band gap of 0.1 eV, equivalent to 12 μm.[4,21] Using TMSb in this temperature range requires extremely high V/III ratios. As a result, expensive TMSb is wasted. Problems also exist using TIPSb in this temperature range: It is necessary to use TIPSb flow rates as high as 1000 sccm because of its low vapor pressure and incomplete decomposition.[13,14] This may lead to nonsaturation of the carrier gas.

In summary, good surface morphology InSb epilayers have been grown using TBDMSb and TMIn at temperatures between 450 °C and 325 °C. The optimum value of V/III ratio increases as the growth temperature is decreased due to the reduced TBDMSb decomposition rate. Using TBDMSb, the growth temperature can be lowered by more than 100 °C as compared to using TMSb, and by about 50 °C as compared to using TIPSb. The InSb growth efficiency is $\sim 10^4$ μm/mole, indicating minimal parasitic reactions between TMIn and TBDMSb. The results show that TBDMSb is superior to both TMSb and TIPSb for growth at temperatures lower than 400 °C.

The financial support for this work was provided by the Office of Naval Research.

[1] G. B. Stringfellow and P. E. Greene, J. Electrochem. Soc. **118**, 805 (1971).
[2] M. J. Cherng, Y. T. Cherng, H. R. Jen, P. Harper, R. M. Cohen, and G. B. Stringfellow, J. Electron. Mater. **15**, 79 (1986).
[3] M. J. Jou, Y. T. Cherng, H. R. Jen, and G. B. Stringfellow, J. Cryst. Growth **93**, 62 (1988).
[4] K. Y. Ma, Z. M. Fang, R. M. Cohen, and G. B. Stringfellow, J. Appl. Phys. **68**, 4586 (1990).
[5] K. Y. Ma, Z. M. Fang, R. M. Cohen, and G. B. Stringfellow, J. Appl. Phys. **70**, 3940 (1991).
[6] C. A. Larsen, S. H. Li, and G. B. Stringfellow, Chem. Mater. **3**, 39 (1991).
[7] T. Fukui and Y. Horikoshi, Jpn. J. Appl. Phys. **20**, 587 (1981).
[8] R. M. Biefeld and G. A. Hebner, Appl. Phys. Lett. **57**, 1563 (1990).
[9] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, New York, 1989), p. 19.
[10] C. A. Larsen, G. B. Stringfellow, and R. W. Gedridge, Jr., Chem. Mater. **3**, 96 (1991).
[11] S. H. Li, C. A. Larsen, G. B. Stringfellow, and R. W. Gedridge, Jr., J. Electron. Mater. **20**, 457 (1991).
[12] S. H. Li and G. B. Stringfellow (unpublished).
[13] C. H. Chen, Z. M. Fang, G. B. Stringfellow, and R. W. Gedridge, Jr., J. Appl. Phys. **69**, 7605 (1991).
[14] G. T. Stauf, D. K. Gaskill, N. Bottka, and R. W. Gedridge, Jr., Appl. Phys. Lett. **58**, 1311 (1991).
[15] D. S. Cao, C. H. Chen, C. W. Hill, S. H. Li, G. B. Stringfellow, D. C. Gordon, D. W. Brown, and B. A. Vaartstra, J. Electron. Mater. **21**, 583 (1992).
[16] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, New York, 1989), pp. 26–28.
[17] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, New York 1989), Chap. 3.
[18] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, New York, 1989), pp. 84–86.
[19] R. S. Wagner, in *Whiskers Technology*, edited by A. P. Levitt (Wiley, New York, 1970), pp. 47–119.
[20] N. I. Buchan, C. A. Larsen, and G. B. Stringfellow, J. Cryst. Growth **92**, 591 (1988).
[21] Z. M. Fang, K. Y. Ma, D. H. Jaw, R. M. Cohen, and G. B. Stringfellow, J. Appl. Phys. **67**, 7034 (1990).